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Synthesis and properties of near-infrared absorbing asymmetric pyrylium–squarylium dyes containing tertiary butyl groups

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Abstract

Asymmetric pyrylium–squarylium dyes (**5a**–**b**) were prepared by direct condensation of squaric acid with two different kinds of heterocycles. Symmetrical dyes **5d–f** were isolated as by-products. Asymmetric dye **5c** was synthesized via the traditional way using monosubstituted squaric acid as the key intermediate. Dyes **5a–f** were characterized with the aid of ^{1}H-NMR, IR, mass spectroscopy and elemental analysis. The dyes exhibit high melting points and absorption maxima in the range of 720–760 nm with high extinction coefficients and higher solubility in organic solvents than other squarylium dyes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Asymmetric squarylium dye; Pyrylium cyanine dye; Solubility; Solvent effect

1. Introduction

The synthesis of squarylium dyes was first reported about 30 years ago [1]. Squarylium dyes are 1,3-disubstituted products synthesized by condensing one equivalent of squaric acid with two equivalents of various types of electron donating carbocycles and heterocycles such as azulene, pyrroles or heterocyclic methylene bases in an azetropic solvent system. Squarylium dyes have attracted much attention because of their potential applications in photoconductor photoreceptor [2], optical recording media [3], organic solar cells [4] and nonlinear optics [5]. Structural modification of dyes is an active area of research for obtaining good properties. This class of cyanine dyes exhibits a sharp absorption with high extinction coefficients in solution in the visible and near-infrared region ($\lambda_{\max}$~600–750 nm, $\epsilon_{\max}$~3×10 cm^{-1} M^{-1}).

However, the majority of a wide range of squarylium dyes belongs to the class of symmetrical cyanine dyes. We reported a novel class of symmetrical squarylium dyes based on 2,6-di-*t*-butylpyrylium [6], but the synthesis of asymmetric squarylium dyes based on 2,6-di-*t*-butylpyrylium has never been reported. As an extension of that work, we now report the synthesis, spectral properties, solubility and solvent effects of asymmetric and symmetrical pyrylium–squarylium dyes that could be obtained via a direct acid route.

Traditionally, symmetrical squarylium dyes are synthesized via one-pot acid route and asymmetric squarylium dyes are obtained through ester route, which leads to more steps and lower yields [7].

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Monosubstituted squaric acid is the key intermediate in the synthesis of asymmetric squarylium dyes. We report a one-pot squaric acid route in synthesis of asymmetric squarylium dyes below, which has fewer steps and higher yields than those do in normal ester route.

2. Results and discussion

2.1. Synthesis of asymmetric pyrylium–squarylium dyes **5** and precursors

Compounds **3a–c** were prepared successfully according to the procedure shown in Fig. 1.

2,6-Di-*t*-butylpyrylium perchlorate was prepared as described in the literature [8], and was then reacted with a carboxylic acid catalyzed by $K_2S_2O_8/Ag^+$ to give **3a–c** as white needles. The melting points of **3a–c** decreased with the increase of the carbon number of the 4-substituted alkyl group. The free radical reaction in this synthesis is a novel method for obtaining different heterocycles [9,10]. The results are summarized in Tables 1 and 2.

Traditionally, asymmetric squarylium dyes cannot be obtained via a direct condensation of squaric acid with heterocycles, but in some cases, the direct reaction through acid route is effective, convenient and high yielding. The procedure used to prepare

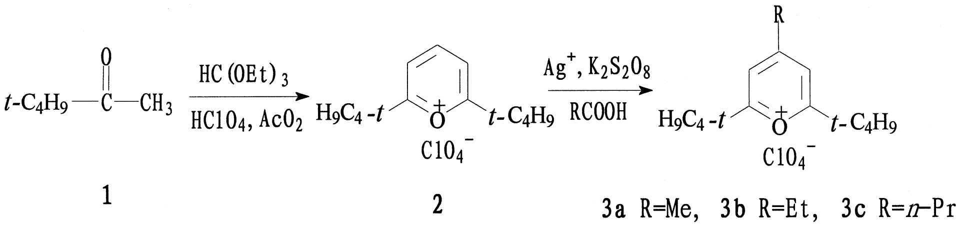

Fig. 1. Illustration of synthesis of 4-alkyl-2,6-di-*t*-butylpyrylium perchlorates **3**.

Table 1
Characterization data for pyrylium perchlorates **3**

Compound	R	Yield (%)	M.p. (°C)	MS (*m*/*z*)	Analysis (%) Found/Calcd C	Analysis (%) Found/Calcd H
3a	Me	59	232–233	207 (m$^+$,100%)	54.56 54.79	7.71 7.56
3b	Et	49	152–154	221 (m$^+$,100%)	55.92 56.14	7.97 7.86
3c	*n*-Pr	35	80-82	235 (m$^+$,100%)	57.51 57.37	8.30 8.13

Table 2
Spectroscopic properties of pyrylium perchlorates **3**

Compound	IR (cm^{-1})	^{1}H-NMR (CDCl$_3$, ppm from TMS)
3a	1632 (s), 1537 (m), 1091 (s), 622 (s)	1.58 (s, 18H), 3.01 (s, 3H), 7.75 (s, 2H)
3b	1630 (s), 1537 (m), 1089 (s), 622 (s)	1.55 (s, 18H), 1.62 (t, 3H), 3.06 (m, 2H), 7.78 (s, 2H)
3c	1633 (s), 1538 (m), 1088 (s), 623 (s)	1.06 (t, 3H), 1.54 (s, 18H), 1.84 (m, 2H), 3.09 (t, 2H), 7.79 (s, 2H)

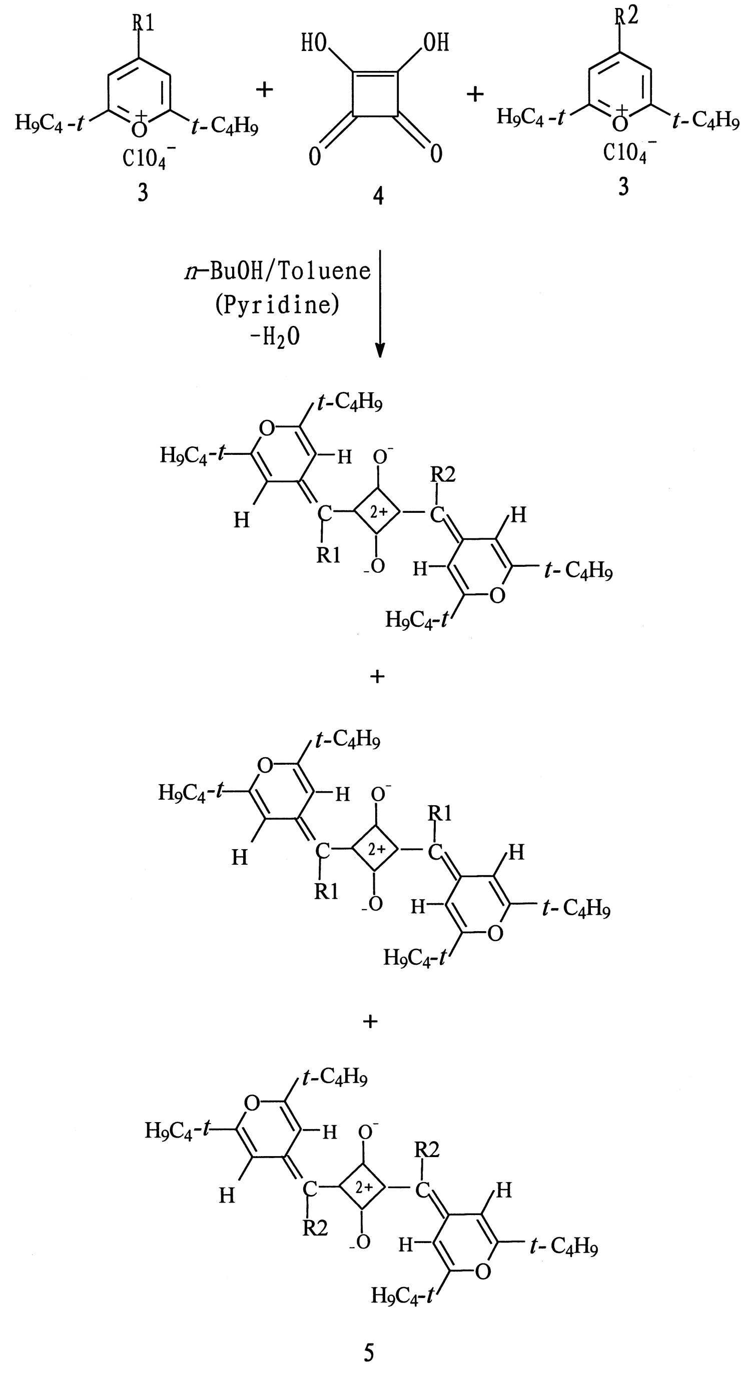

Fig. 2. Illustration of synthesis of asymmetric squarylium dyes **5** via direct reaction.

the asymmetric squarylium dyes is shown in Fig. 2. The characterization data and spectroscopic data are summarized in Tables 3 and 4. A mixture of two different pyrylium perchlorates (**3**) and squaric acid (**4**) in *n*-butanol/toluene containing pyridine as catalyst was refluxed for 10 h to give dyes **5a–c**. Asymmetric pyrylium–squarylium dyes were separated from two other symmetrical dyes, which were synthesized at the same time, by column chromatography. In spite of the same equivalent of two pyrylium perchlorates, the yields of dye **5e** and **5f** are much lower than the yield of **5d**, which may be attributed to the larger steric effect of 4-substitued alkyl group in **5e** and **5f**.

Though dye **5c** was detected by HPLC–MS instrument, it could not be separated from **5e** and

Table 3
Characterization data for squarylium dyes **5**

Compound	R1	R2	Yield (%)	M.p. (°C)	MS (*m*/*z*)	Analysis (%) Found/Calcd C	H
5a	H	Me	38	237–239	504 (m^+, 100%)	78.21 78.51	8.93 8.79
5b	H	Et	31	214–215	518 (m^+, 100%)	78.51 78.76	8.99 8.94
5c	Me	Et	17[a]	243–246	532 (m^+, 100%)	78.61 78.89	9.23 9.09
5d	H	H	45[b]	240–242	490 (m^+, 100%)	78.04 78.31	8.71 8.63
5e	Me	Me	4.1	269–272	518 (m^+, 100%)	78.43 78.71	8.96 8.94
5f	Et	Et	3.5	222–224	547 (m^+ + 1100%)	79.22 79.06	9.30 9.22

Table 4
Spectroscopic properties of squarylium dyes **5**

Compound	IR (cm^{-1})	λ_{max} (nm) log ϵ	(CHCl$_3$)	^{1}H-NMR (CDCl$_3$, ppm from TMS)
5a	1642 (s), 1598 (m), 1566 (w), 1474 (m), 1428 (s), 1324 (w)	739	5.48	1.29 (s, 36H), 2.30 (s, 3H), 5.83 (s, 1H), 6.15 (s, 1H), 6.37 (s, 1H), 8.50 (s, 1H), 8.98 (s, 1H)
5b	1640 (s), 1601 (s), 1542 (w), 1470 (m), 1428 (w), 1333(m)	736	5.53	1.15 (t, 3H), 1.31 (s, 36H), 2.91 (m, 2H), 5.82 (s, 1H), 6.18 (s, 1H), 6.40 (s, 1H), 8.51 (s, 1H), 8.93 (s, 1H)
5c	1635 (s), 1591 (m), 1565 (w), 1458 (s), 1414 (s), 1311 (w)	761	5.36	1.13 (t, 3H), 1.32 (s, 36H), 2.31 (s, 3H), 2.92 (m, 2H), 6.21 (s, 1H), 6.41 (s, 1H), 8.56 (s, 1H), 8.95 (s, 1H)
5d	1634 (s), 1586 (w), 1565 (w), 1458 (s), 1415 (s), 1314 (s)	711	5.52	1.20 (s, 18H), 1.27 (s, 18H), 5.80 (s, 2H), 6.18 (s, 2H), 8.60 (s, 2H)
5e	1639 (s), 1593 (m), 1564 (m), 1415 (s), 1303 (w), 1564 (m)	763	5.39	1.26 (s, 36H), 2.20 (s, 6H), 6.25 (s, 2H), 8.75 (s, 2H)
5f	1633 (s), 1586 (w),1565 (w), 1458 (s), 1414 (s), 1313 (w)	759	5.35	1.11 (t, 6H), 1.32 (s, 36H), 2.91 (m, 4H), 6.36 (s, 2H), 8.70 (s, 2H)

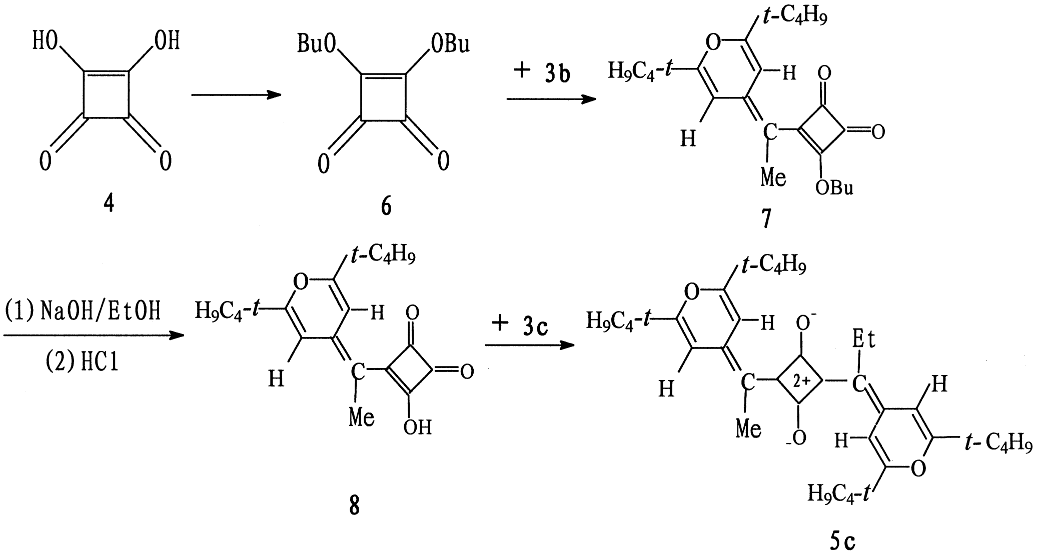

Fig. 3. Illustration of synthesis of asymmetric squarylium dye **5c** via ester route.

5f by column chromatography because the R_f values of **5c**, **5e** and **5f** were very close. Dye **5c** was prepared by the general way as shown in Fig. 3. Similar reactions have already been described previously [7,11]. This procedure leads to more steps and lower yield (see Fig. 3 and Table 3).

2.2. Structure elucidation of the squarylium dyes 5

The structure elucidation of the squarylium dyes **5** was achieved mainly with the aid of IR, UV/VIS, ^{1}H-NMR and elemental analysis as well as electronic impact mass spectroscopy. Spectroscopy data are summarized in Table 4.

The pyrylium–squarylium dyes **5** are all metallic shining, high melting compounds, yet with higher solubility in many organic solvents than other squarylium dyes because each molecule contains four tertiary butyl groups. The solubility is, to some extent, an important criterion for the use of these squarylium dyes in near-infrared region. The solubility of dyes **5** in different kinds of alcohol is shown in Table 5.

All the symmetrical and asymmetric pyrylium–squarylium dyes exhibit intense and sharp absorption bands in the near-infrared region. Visible absorption data for dyes **5a–f** are summarized in Table 4. In chloroform their absorption maxima as well as their extinction coefficients depend on the substituent groups linked to polymethine chain.

Like the IR spectra of other squarylium dyes, the IR spectra of these squarylium dyes **5** do not show any evidence of carbonyl absorption in the region of 1680~1800 cm^{-1}, but exhibit strong absorption bands in the region of 1630~1640 cm^{-1}, indicating the strong C=C stretching in the four-membered ring system.

Solvent effects of dyes **5** were studied. As the solvent polarity increased, a hypsochromic shift was observed (i.e. negative solvatochromism). The λ_{max} of visible spectra in different solvents is listed in Table 6.

From the solvatochromism and IR spectra, it was concluded that structure of dye **5** is more polar, as shown in Fig. 4. The two ending pyrylium rings show quinonoid structure.

Table 5
Solubility of squarylium dyes **5** (g/l, 25°C)

Solvent	5a	5b	5c	5d	5e	5f
Ethanol	8.9	15.6	5.4	51.1	0.4	11.6
i-Propyl alcohol	12.1	18.0	6.8	30.4	1.1	15.7
n-Butanol	14.3	29.5	10.7	75.4	2.7	40.0

Table 6
Solvent effects on visible spectra of squarylium dyes **5** (λ_{max}, nm)

Solvent	E_T (kJ/mol)	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**
$CHCl_3$	163	739	736	761	711	763	759
EtOH	217	727	725	750	702	753	748
n-C_6H_{14}	129	741	737	751	711	763	757
AcOH	214	724	720	745	696	746	743
DMF	183	738	734	763	718	768	762

^{1}H-NMR spectra of the asymmetric squarylium dyes **5a–c** show a doublet around 6.30 ppm and another doublet around 8.70 ppm for the protons of two pyrylium rings, whereas the same appear as a singlet with a chemical shift of 6.20 and 8.70 ppm in the symmetrical dyes **5d–f**.

In symmetrical squarylium dyes (R1 = R2), chemical environment of H^b and H^d or H^a and H^c is equal. So there are only two singlets which are near 6.20 ppm (H^b, H^d) and 8.70 ppm (H^a, H^c) area. The difference of these two singlets was ever explained with the aid of X-ray single crystal data [12]. The chemical shifts of H^a and H^c are influenced by atom O, as shown in Fig. 4. There is a short intramolecular contact between H^a (or H^c) and O in which the geometry of C–H··· contact is H···O = 2.008 Å and the angle at H = 148.2°. This strong intermolecular interaction causes △δ (H^a, H^b) = △δ (H^c, H^d)≈2.50 ppm. But in asymmetric dyes, the observed splitting of the two heteroaromatic protons of asymmetric squarylium dye **5b** [as an example, R1 = H, R2 = Et, δ(H^a) = 8.92 ppm, δ(H^c) = 8.55ppm] into doublets is related to the different steric effect of R1 and R2. A more detailed study on the steric effect of substituent group on the ^{1}H-NMR spectra of asymmetric squarylium dyes is being performed with the aid of X-ray single crystal analysis and will be reported later.

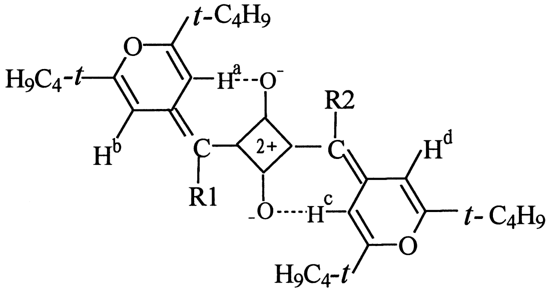

Fig. 4. Structure of pyrylium–squarylium dye.

3. Experimental

3.1. General

Melting points were determined using a Yanaco Micro Melting Point Apparatus and are uncorrected. The visible and IR spectra were measured using a Perkin-Elmer UV/VIS Lambda 20 and a Perkin-Elmer FTIR Paragon 1000 spectrophotometer (KBr), respectively. Elemental analyses were recorded on a MOD-1106 and mass spectra (EI) were recorded on a HP 5989A. ^{1}H-NMR spectra were taken with a Gemini-2000 (300 HZ, Varian Ltd.) instrument at room temperature.

3.2. Materials

Squaric acid was prepared as described in literature [13]. Pinacolone (t-butyl methyl ketone), acetic acid, propanoic acid and n-butyric acid were used without further purification. Organic solvents were reagent grade and used after distillation.

3.3. Synthesis of asymmetric pyrylium–squarylium dyes 5

3.3.1. Preparation of 4-alkyl-2,6-di-t-butylpyrylium perchlorate (3a–c) (general method)

Perchloric acid (70%, 14.4 g, 100.3 mmol) was added dropwise to ice-cooled acetic anhydride (40 ml) under stirring. The solution was added to an ice-cooled and well-stirred mixture of pinacolone (10.0 g, 100 mmol) and triethyl orthoformate (50 ml). The reaction mixture was poured into ether(~300 ml). The collected solid was purified by crystallization from ethanol. The salt **2** was obtained in 57% yield and melted at 230°C.

A two-phase solution (60 ml dichloromethane and 120 ml distilled water) of acetic acid (4.5 g, 75 mmol), 2,6-di-t-butylpyrylium perchlorate (**2**) (4.4 g, 15 mmol), $K_2S_2O_8$ (6.1 g, 225 mmol) and $AgNO_3$ (135 mg, 0.79 mmol) was heated for 4 h at

30°C. The reaction mixture was cooled to room temperature and extracted with dichloromethane, washed with 5% $HClO_4$ once and water twice.

After being dried by $CaCl_2$, the solution was concentrated to about 5 ml and added to 100 ml ether. The residue was crystallized from ethanol–water to give fine needles (**3a**) (2.7 g, 59%). Ethyl, *n*-propyl substituted compounds were obtained via a similar procedure. Relevant data for compounds **3a–c** are summarized in Tables 1 and 2.

3.3.2. Preparation of pyrylium–squarylium dyes (5a–c) (general method)

4-Methyl-2,6-di-*t*-butylpyrylium perchlorate (**3a**) (613 mg, 2 mmol), 4-ethyl-2,6-di-*t*-butylpyrylium perchlorate (**3b**) (641 mg, 2 mmol) and squaric acid (228 mg, 2 mmol) were heated under reflux for 10 h in a mixture of *n*-butanol/toluene (5:1/v:v) containing 0.36 ml pyridine. Water was removed azeotropically. The reaction mixture was evaporated and submitted to column chromatography on silica gel (100–200 mesh) using dichloromethane–ethyl acetate (16:10/v:v) as eluent, to give eluent dyes **5e**, **5a** and **5d** in sequence. Dye **5b** was obtained using a similar procedure. Symmetrical dyes **5d–f** were isolated as by-products. Dye **5c** could not be separated from dyes **5e** and **5f** by column chromatography though it could be detected by HPLC–MS instrument and had to be synthesized via the procedure as shown in Fig. 3.

3.3.3. Preparation of pyrylium–squarylium dyes (5c)

Di-*n*-butylsquarate (**6**) was prepared by refluxing a mixture of squaric acid, *n*-butanol and toluene and was then isolated by vacuum distillation. Water was removed azeotropically. **7** was obtained by condensation of 4-ethyl-2,6-di-*t*-butylpyrulium (**3b**) (801 mg, 2.5 mmol) with di-*n*-butylsquarate (452 mg, 2 mmol) in 5 ml ethanol containing 0.4 ml triethylamine and was purified by column chromatography with petroleum ether–ethyl acetate (12:1/v:v) as eluent. **8** was obtained through hydrolysis of **7** and used without further purification.

A portion (1 mmol) of **8** and 1 mmol of **3c** were heated for 10 h under reflux in 10 ml *n*-butanol. Purification was achieved by column chromatography with dichloromethane–ethyl acetate (16:10/v:v) as eluent. Yield and relevant data are summarized in Tables 3 and 4.

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